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Report to Dr. F. Smidt, Naval Research Laboratory, Washington, D.C.

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Evaluation of the use of sputter profiling with XPS or AES for the study of surface carburization resulting from high energy (>20 keV) ion implantation.

#### Introduction

We have previously used Auger depth profiling with Xe ion etching to determine the extent of carburization resulting from ion implantation. An ongoing study with Dr. Ken Grabowski will be described in the next report. In this report we have investigated the possibility of surface carburization resulting from the low energy ion bombardment associated with sputter profiling.

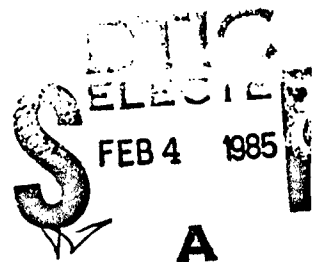
When a sample is analyzed by AES or XPS a surface contaminant layer of carbonaceous material is always observed. The source of the contamination may be external and/or vacuum related. The following are likely sources:-

- \*Atmospheric,
- \*Cleaning solvents,
- \*Rotary pump oil during initial pump down)
- \*Diffusion pump fluid (polyether), and
- \*Out-gassing of anodes and filaments.

The carbon contamination layer has been examined as a source of carbide formation at the near surface region of the substrate of a high purity Cr sample. The influence of the Xe ion acceleration potential, the amount of carbon contamination and the thickness of the surface oxide layer on the

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amount of carbide formed was determined.

In the first stage of this work a stationary 5 micron electron beam of 3 keV and 20 microamps was used to detect the carbon KLL spectra obtained from the surface oxide of a chromium sample. On monitoring the change in C signal peak-to-peak height over a period of 1000 secs, the position of the beam was then moved to an adjacent location and the KLL line monitored for a further 1000 secs. Figure 1 shows the effect of pressure on the rate of C accumulation. The higher pressure was achieved by back-filling with Xe. The first location of the e-beam shows that C builds up in the region analyzed. The lower carbon accumulation in the adjacent region implies that C build-up is largely due to surface migration as is often found in transmission electron microscopy. At the higher pressure where carbon contamination is greater the higher arrival rate of C washes out the influence of surface migration as indicated by the closeness of the two plots in Figure 1b.

It is relevant to note at this point that we can clearly distinguish between C as a hydrocarbon and carbide either by the e-beam or X-ray induced C KLL Auger spectra as shown in Figures 2 and 3 respectively.

Xe profiling at 3 keV was carried out on a Cr sample and the results are shown in Figure 4a. The C depth profile indicates the presence of hydrocarbon throughout the sputtering of the oxide layer and presence of a carbide within the metal phase. The peak-to-peak heights of the carbide spectra are higher than for the hydrocarbon resulting in an elevation in the depth profile. Continued etching results in complete removal of the carbide. Recontamination led to further carbide formation resulting from the sputter profiling. This is depicted in Figure 4b.



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These results indicate that Xe ion bombardment at 3 keV results in both sputtering and ion beam mixing of the surface carbon. It is apparent from the depth profiles of Figures 5 & 6 that reducing the acceleration potential of Xe to 2 or 1 keV does not reduce the probability of carburization occurring. For an oxide layer of approximately 1 nm the C species can readily enter the metal phase before sputtering has appreciably lowered the C concentration. A thicker surface oxide film should reduce the amount of C reaching the metal-oxide interface and consequently the amount of carbide formed. To illustrate this point a thick oxide film was formed on the Cr sample surface by oxidation at 900°C for 2 hours. Figure 7 shows the resulting depth profile compiled for this sample. It is clearly seen that carbide formation does not occur because entrapment of C in the oxide layer is such that on sputtering of the oxide layer all of the carbon is essentially removed before it can enter the metal.

Since most ion implanted surfaces have oxide layers of the order of the penetration range of the low energy sputter ion species an alternative means must be sought to remove the surface C contaminant layer if carburization due to the implantation process is to be studied. In this work care was taken to employ a high mass element such as Xenon in order to lower depth of penetration by the sputter ion. It is more common to use Argon ions which show in Figure 8 to be more efficient at 2 keV in enabling the surface C to reach the metal substrate.

A similar study was carried out for pure Fe samples in the same way carburization was found to result from auger depth profiling as shown in Figure 9. It is therefore concluded that AES or XPS depth profiling is not suitable for the analysis of ion implantation-induced carburization. Similarly SIMS depth profiling is also unsuitable for this aspect of analysis unless isotope doping is employed.

Polarization studies of Fe implanted with Cr in UHV and CO.

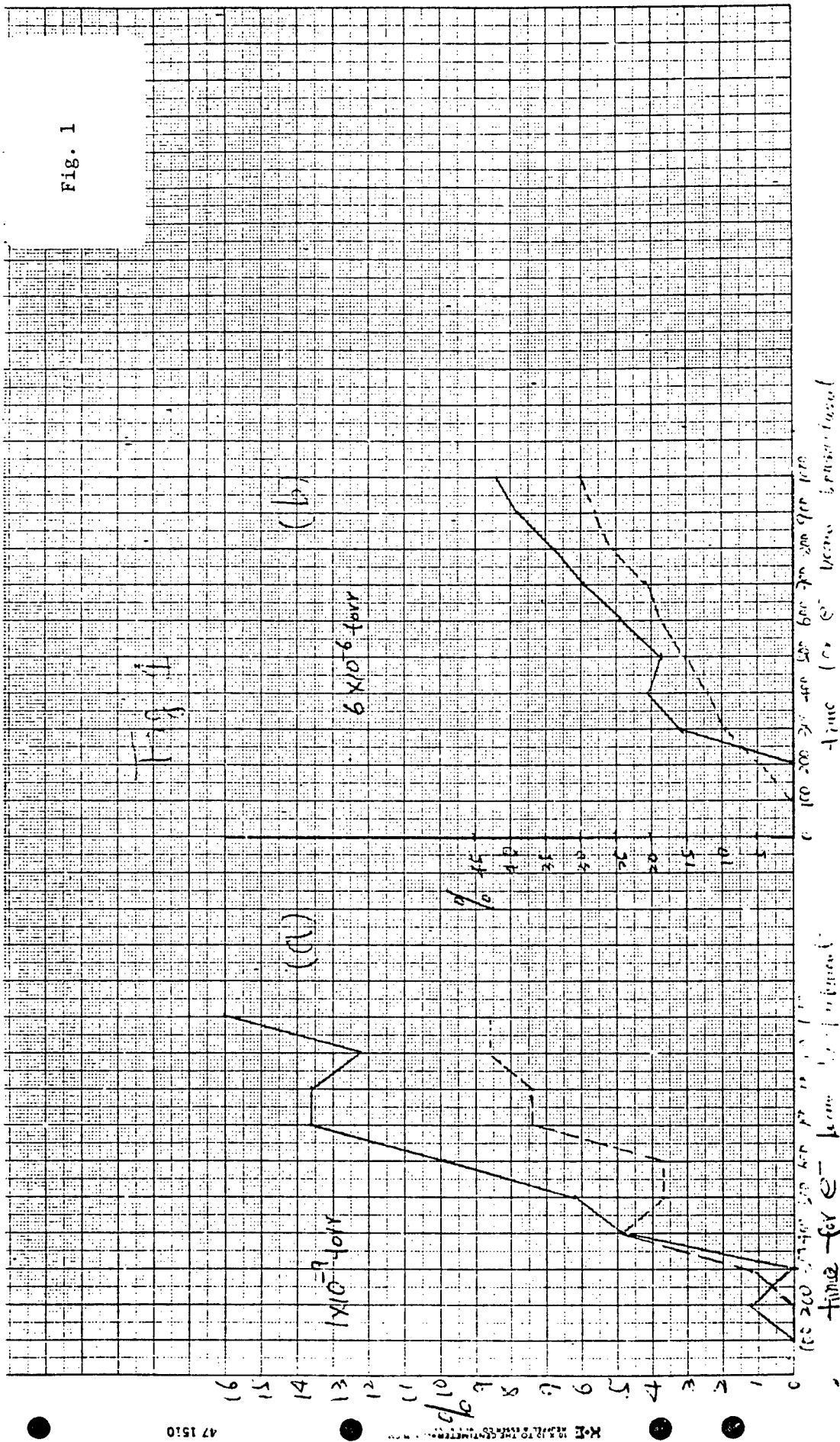
We also report the results of polarization studies of pure Fe and Cr implanted Fe in a pitting solution containing deaerated 0.01M NaCl buffered to pH 6. The polarization curves are shown in Figures 10-14. The following final breakdown potentials were observed:-

SAMPLE	(mV vs SCE)	COMMENTS
Fe	-580	---
Cr->Fe (UHV)	-100	C-C
Cr->Fe (UHV)	-220	C-C
Cr->Fe (UHV)	-240	C-C
Cr->Fe (CO)	-580	---
Cr->Fe (CO)	-190	---

\*C-C = Crevice Corrosion

Three samples revealed large anodic current maxima associated with crevice corrosion under the epoxy mask applied to the samples. The anodic maxima represent the inhibition of crevice corrosion in much the same way as has been reported for pitting. (W. Schwenk Corrosion 20, 129t (1964)). Pitting however is more localized than crevice corrosion attack and would undoubtedly be difficult to inhibit since even shallow pitting would eventually lead to galvanic attack at the Fe-rich base of the pit. The few samples examined showed a mixed behavior. The two Cr implants carried out in the CO environment produced in one case the same breakdown potential as pure Fe and in the other case the second best resistance to localized corrosion. Clearly more testing should be planned.

Fig. 1



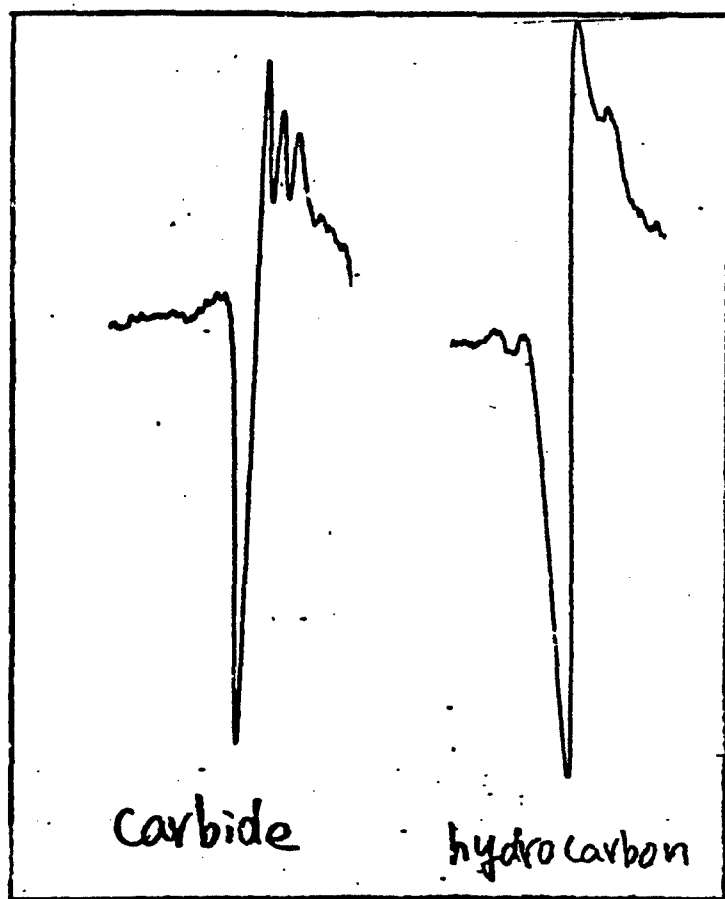
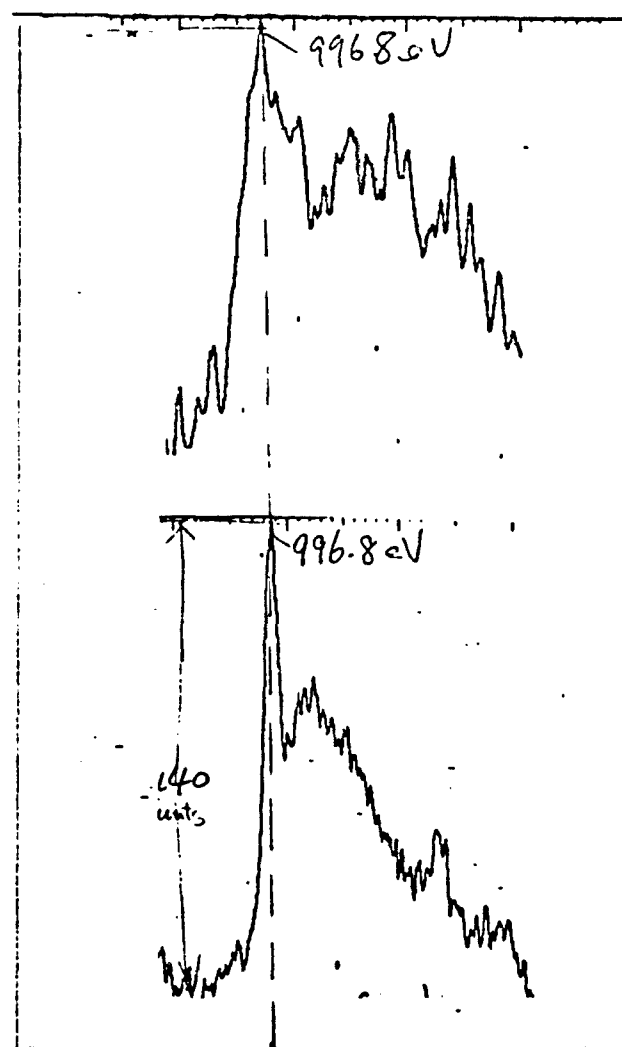


Fig. 2

Fig. 3



hydrocarbon

Carbide.

996.8 eV

Binding energy →

Fig 4(a)

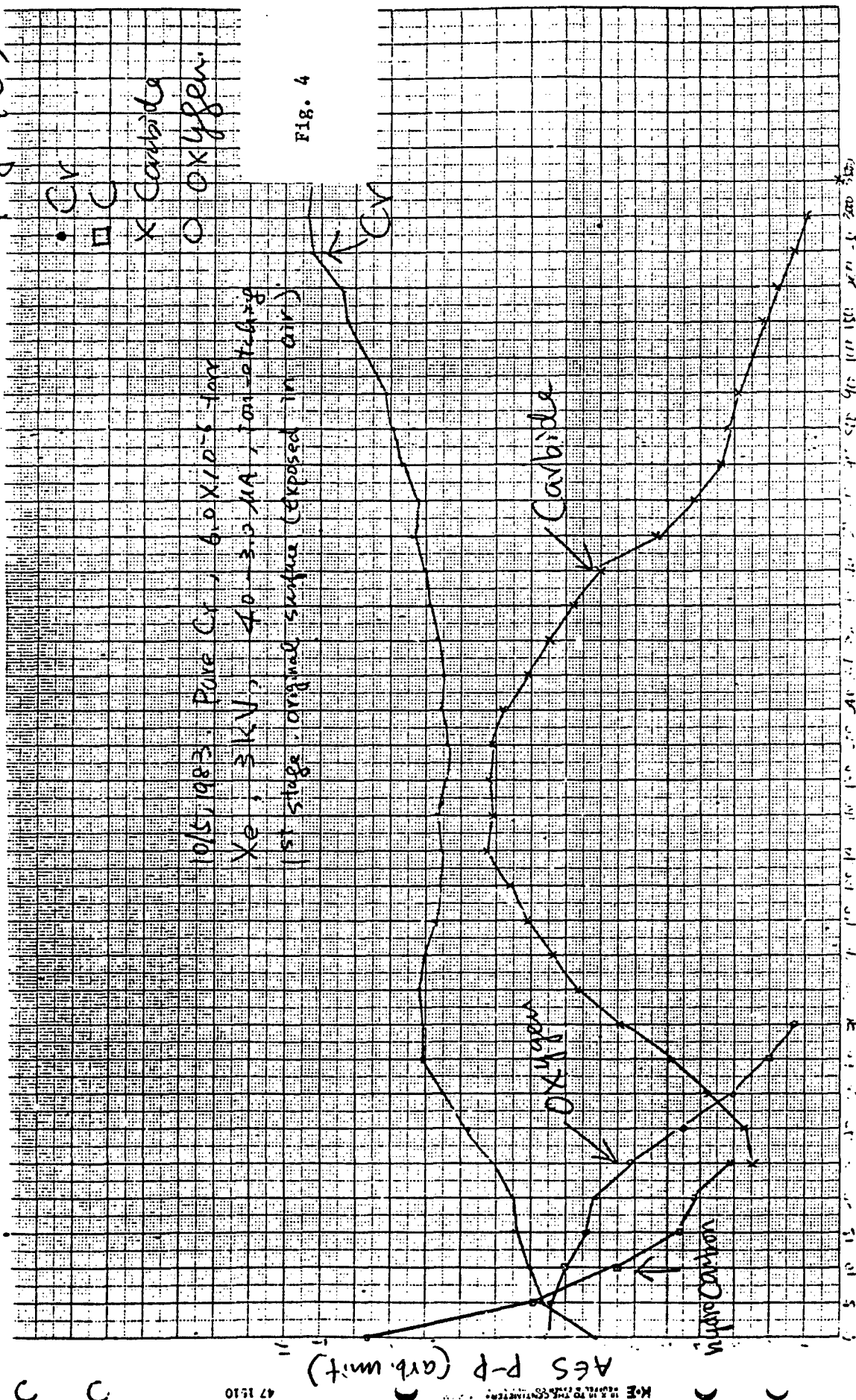


Fig. 4

10/5/1983: Pure Cr, 6.0 X 10<sup>-6</sup> Torr  
Xe, 3 kV, 40-300  $\mu$ A, ion-etching  
1st stage: original surface (exposed in air)

Ton etching (sec) time

AES P-P (arb. unit)

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Fig 4(b)

0/5, 1983. Pure Cr,  $6.0 \times 10^{-6}$  wt %  
Xe, 3KV, 4.0 - 3.0  $\mu$ A, 101 - picking

2nd stage: After capsule was removed completely by ion-sticking,  
recontaminated the sample again in the preparation chamber.  
(Closed off-gas pump, and open rotary pump. To vacuum  
was kept at  $10^{-5}$  torr or higher.) for 20 min.

AMS R-P (arb. unit)

0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000

ion-sticking time (sec)

AES P-P. (arb. unit)

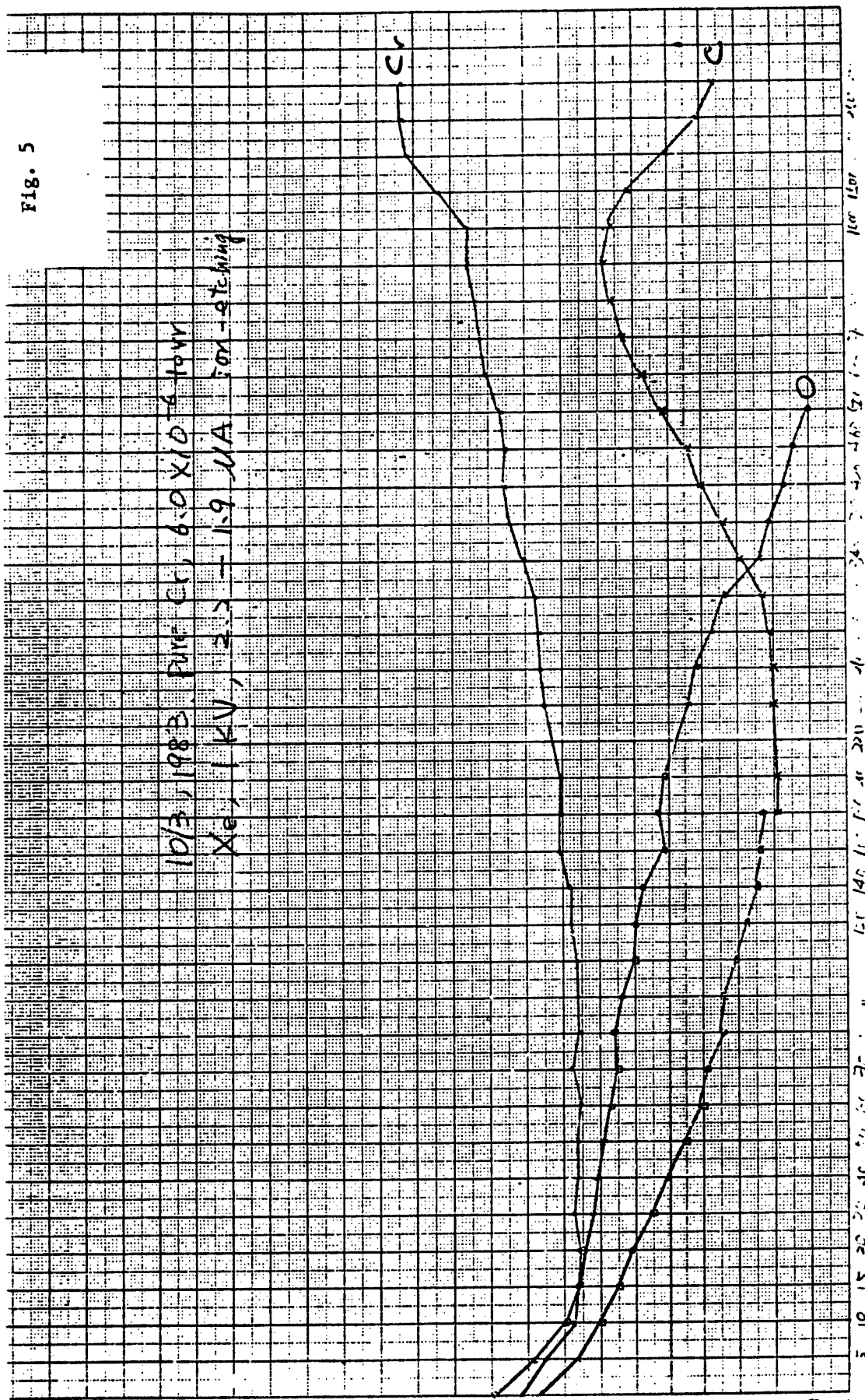
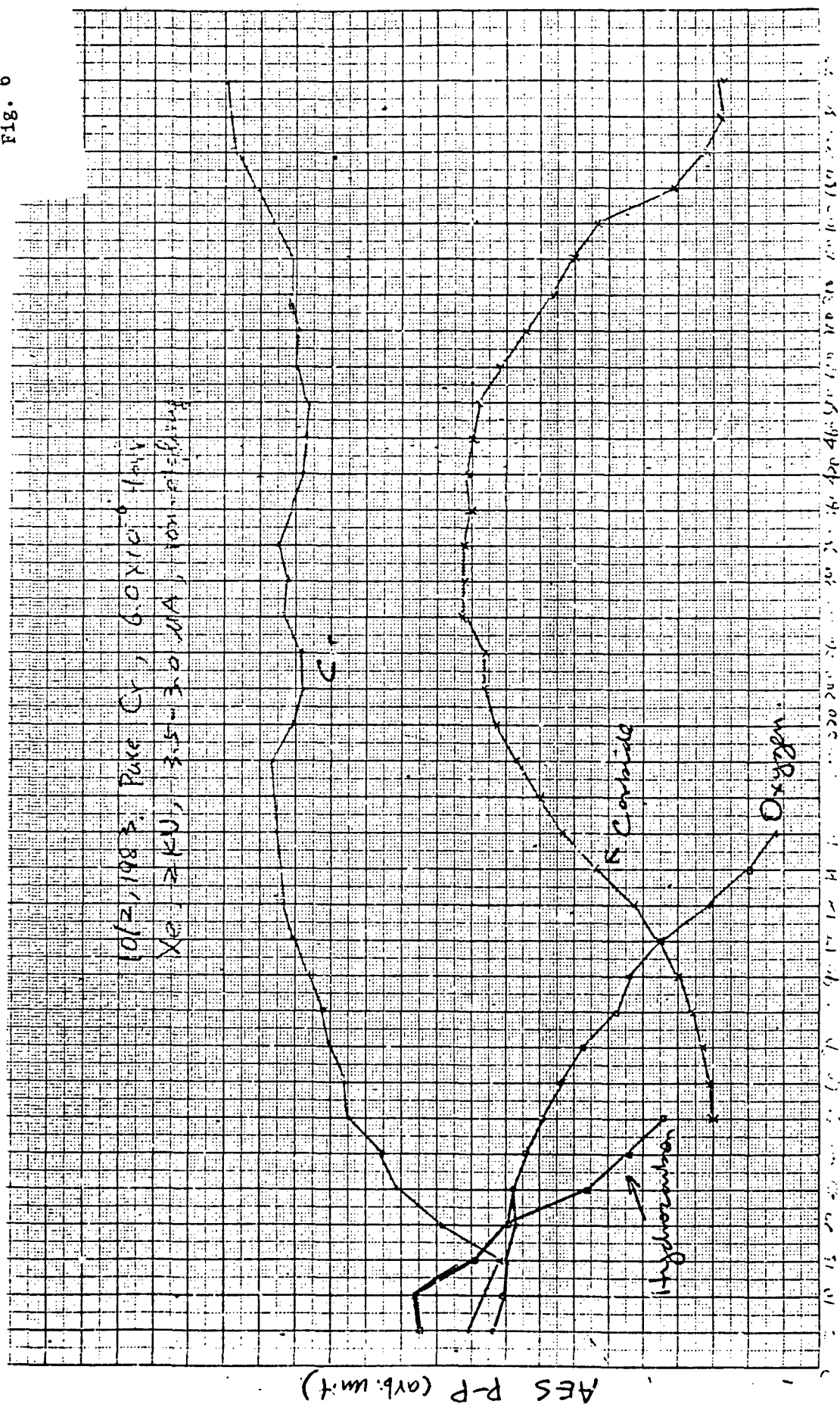


Fig. 5

11/10/83, 1983, Purif Cr,  $6.0 \times 10^{-6}$  Torr  
Xe, 1 kV, 2.5 - 1.9  $\mu$ A Ion-gating

ton-ethyl true (see).

Fig. 6



Ion-etching time (sec)

Fig. 7

9/30, 1983. Pure Cr.  $6.0 \times 10^{-6}$  Torr  
 Xe, 2 kV, 2.5 - 3.0  $\mu$ A; for etching  
 Cr heated at 900°C for 2 hrs in atmosphere  
 to form Cr<sub>2</sub>O<sub>3</sub> on the surface.

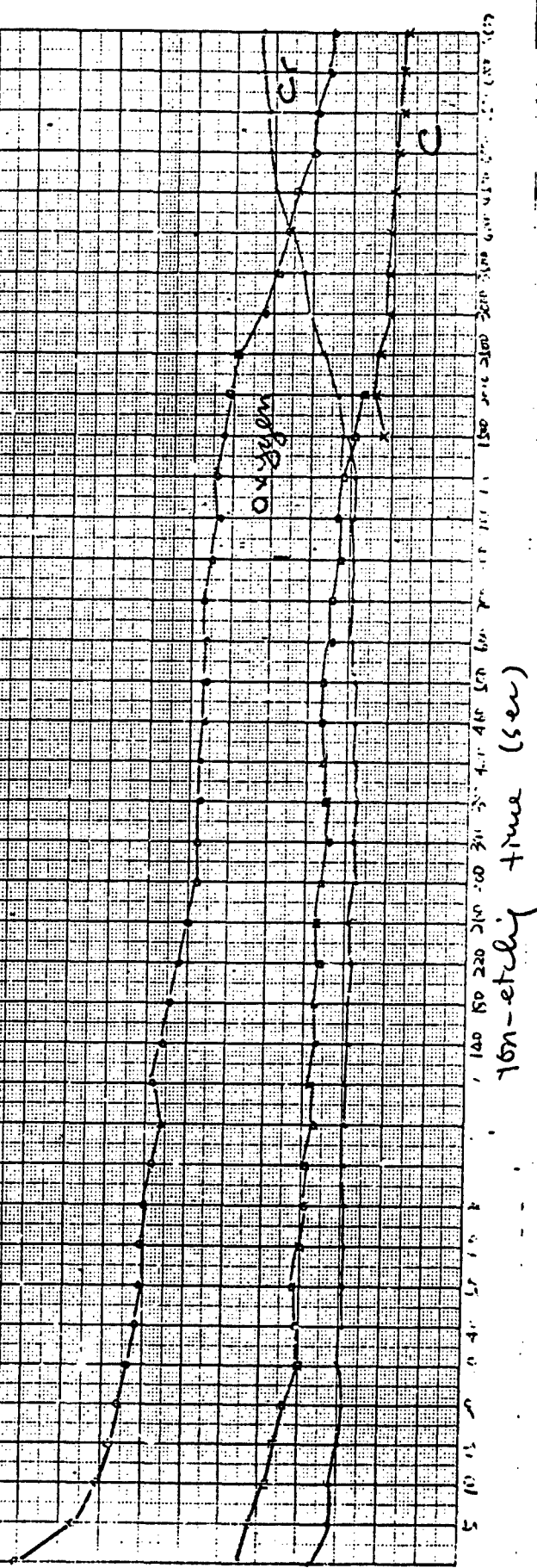
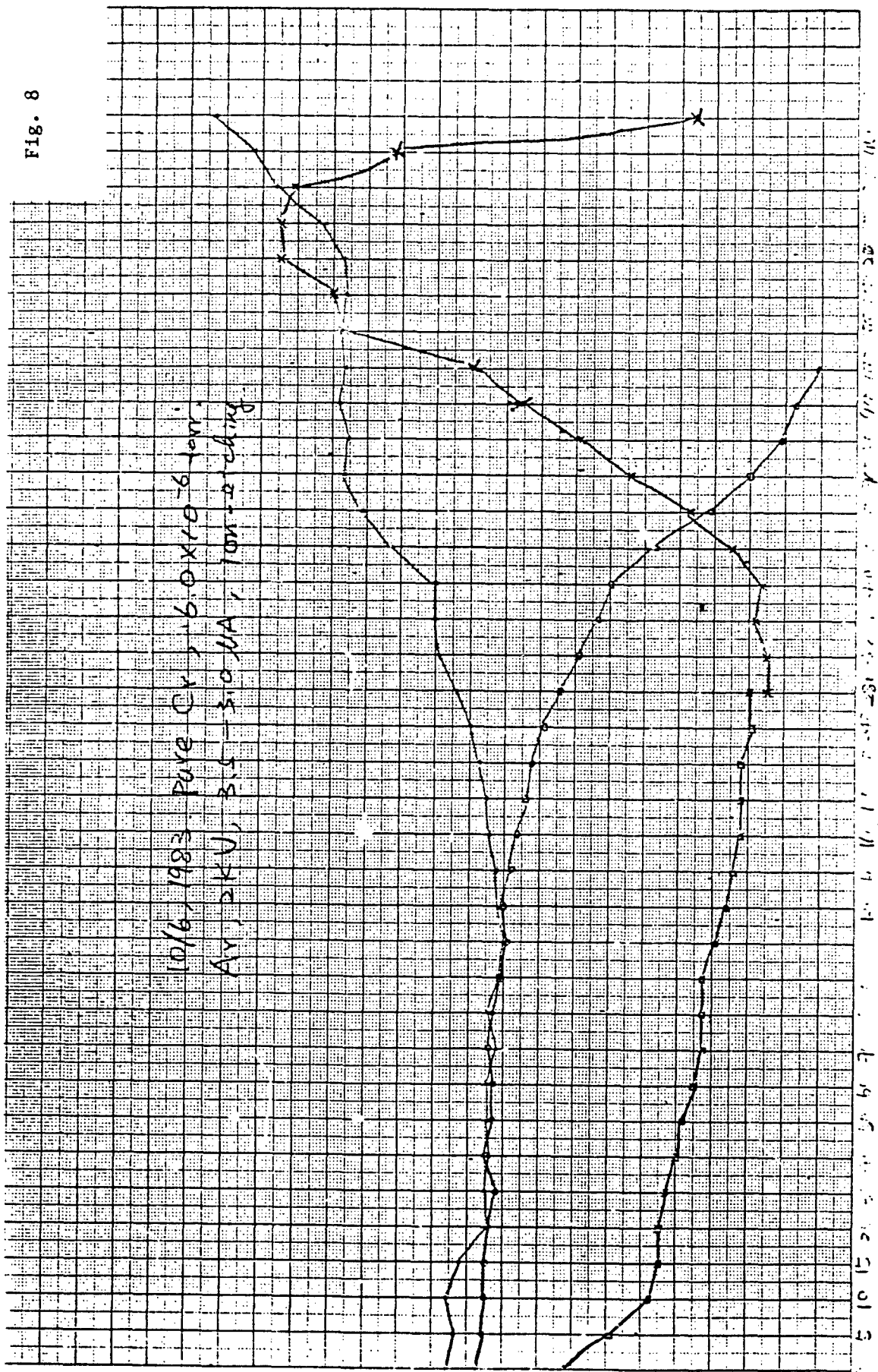


Fig. 8

10/6/1983 Pure Cr 2.6-0.1x10<sup>-6</sup> m.  
 Av, 2KV, 3.5-3.0 uA, 10m-etching.



ion-etching time (sec)

Fig. 9

9/12, 1983, Pure Fe,  $6 \times 10^{16}$   $\text{H}^+$ ,  $3 \text{ MV}$ ,  $3 \text{ cm} \times 1 \text{ cm}$   
 $\text{Xe}$ ,  $161 \text{ e}^-$   $\text{d} \times 10^4$

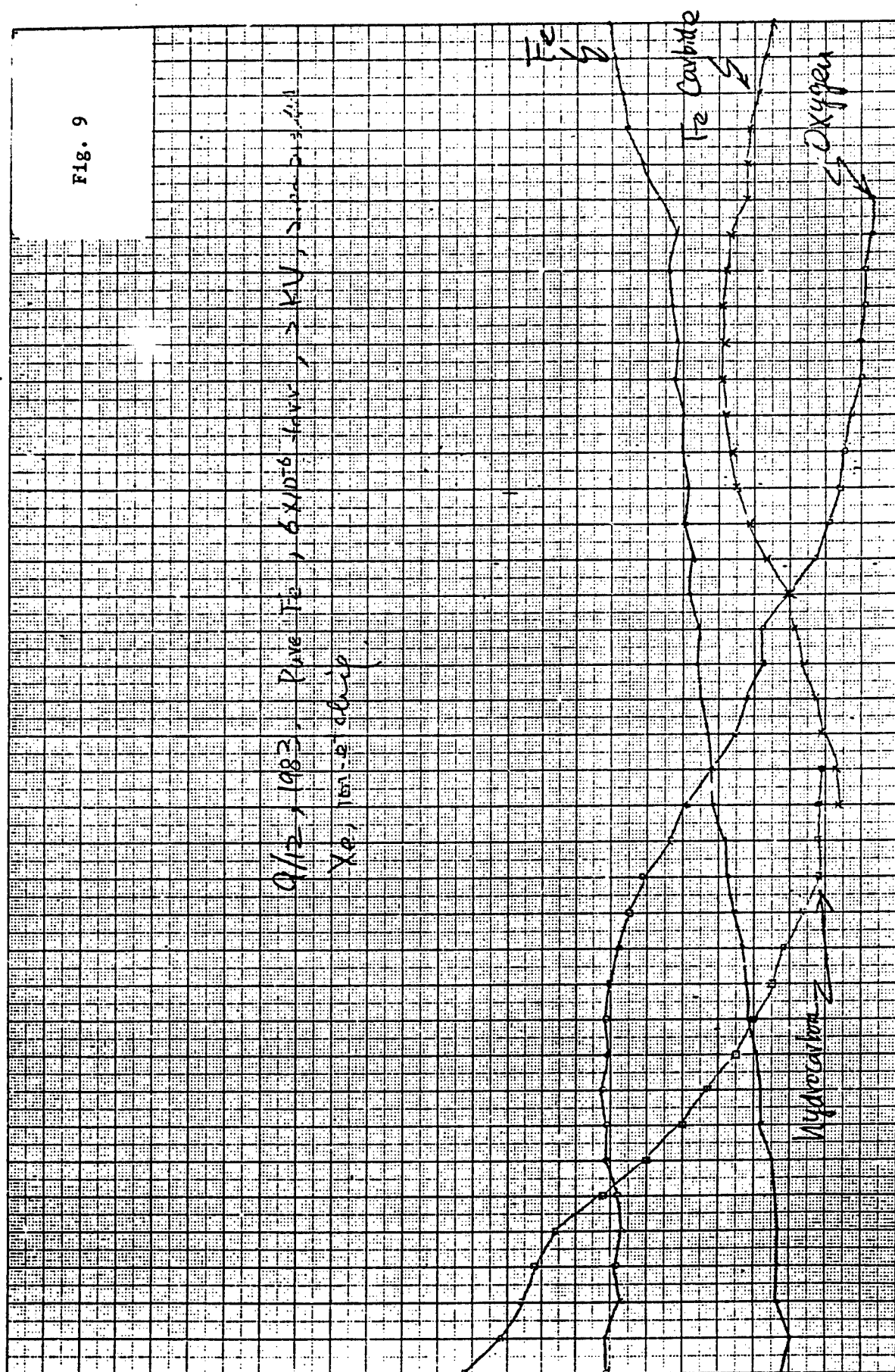


Fig. 10

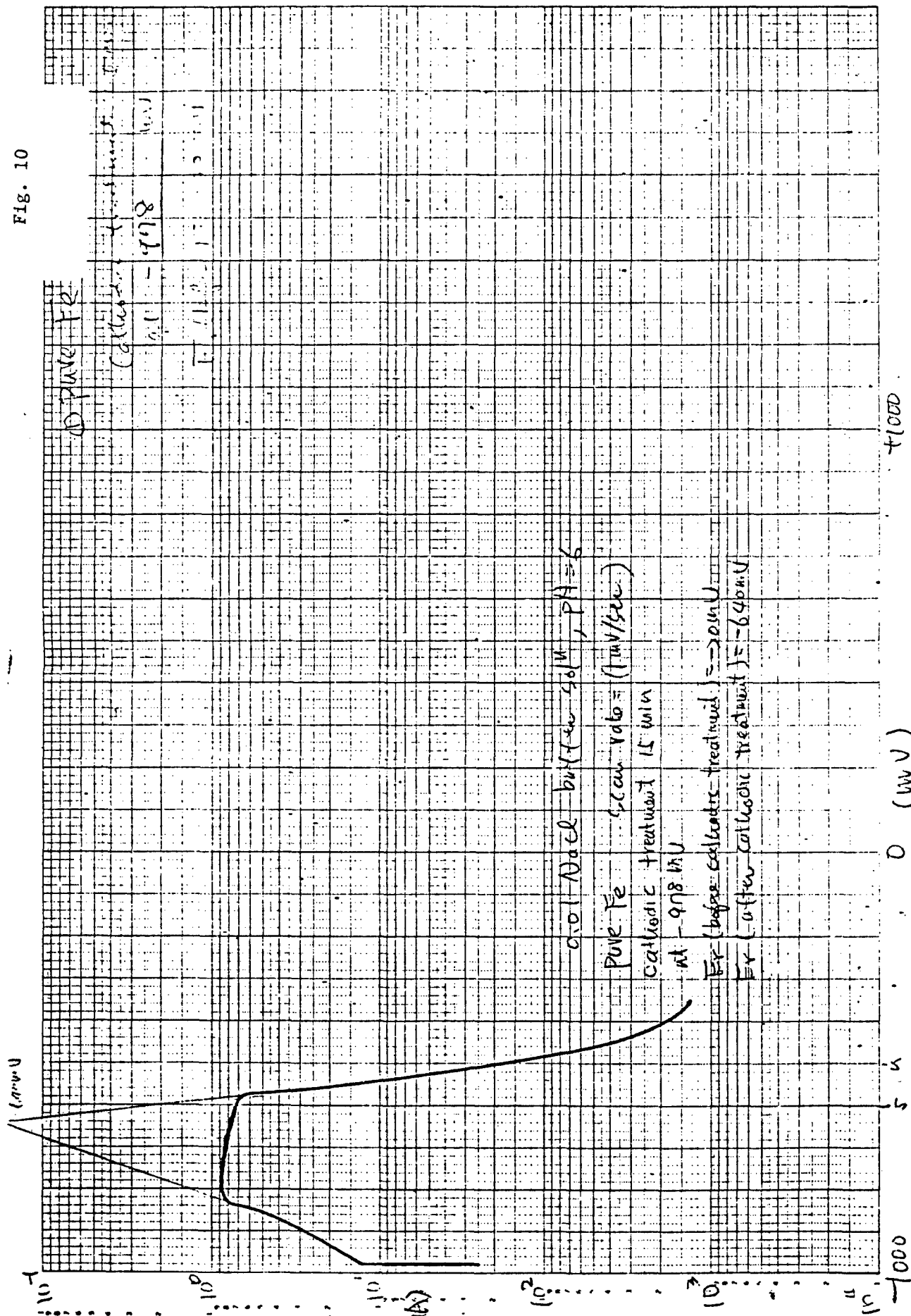




Fig. 12

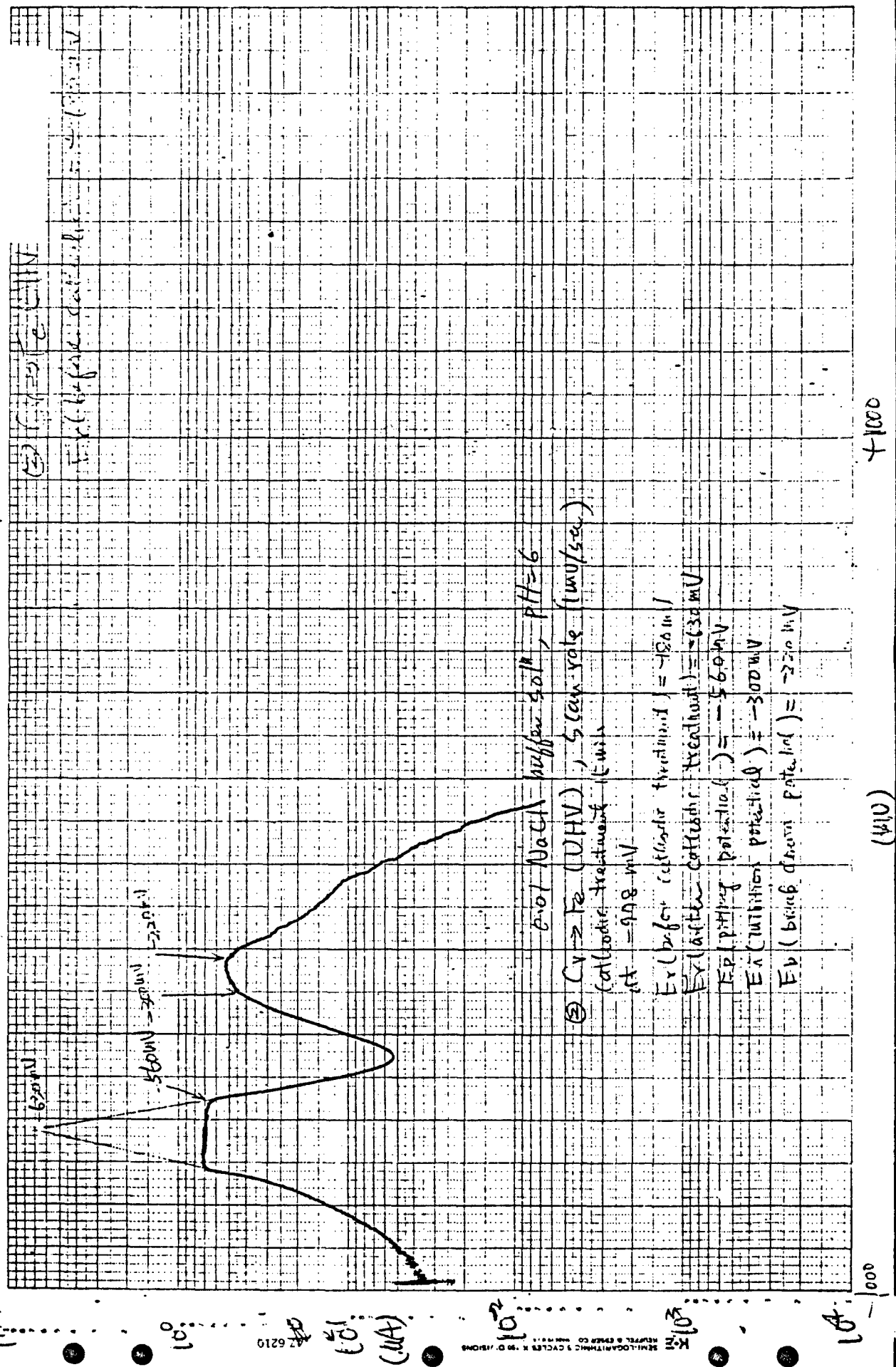


Fig. 13

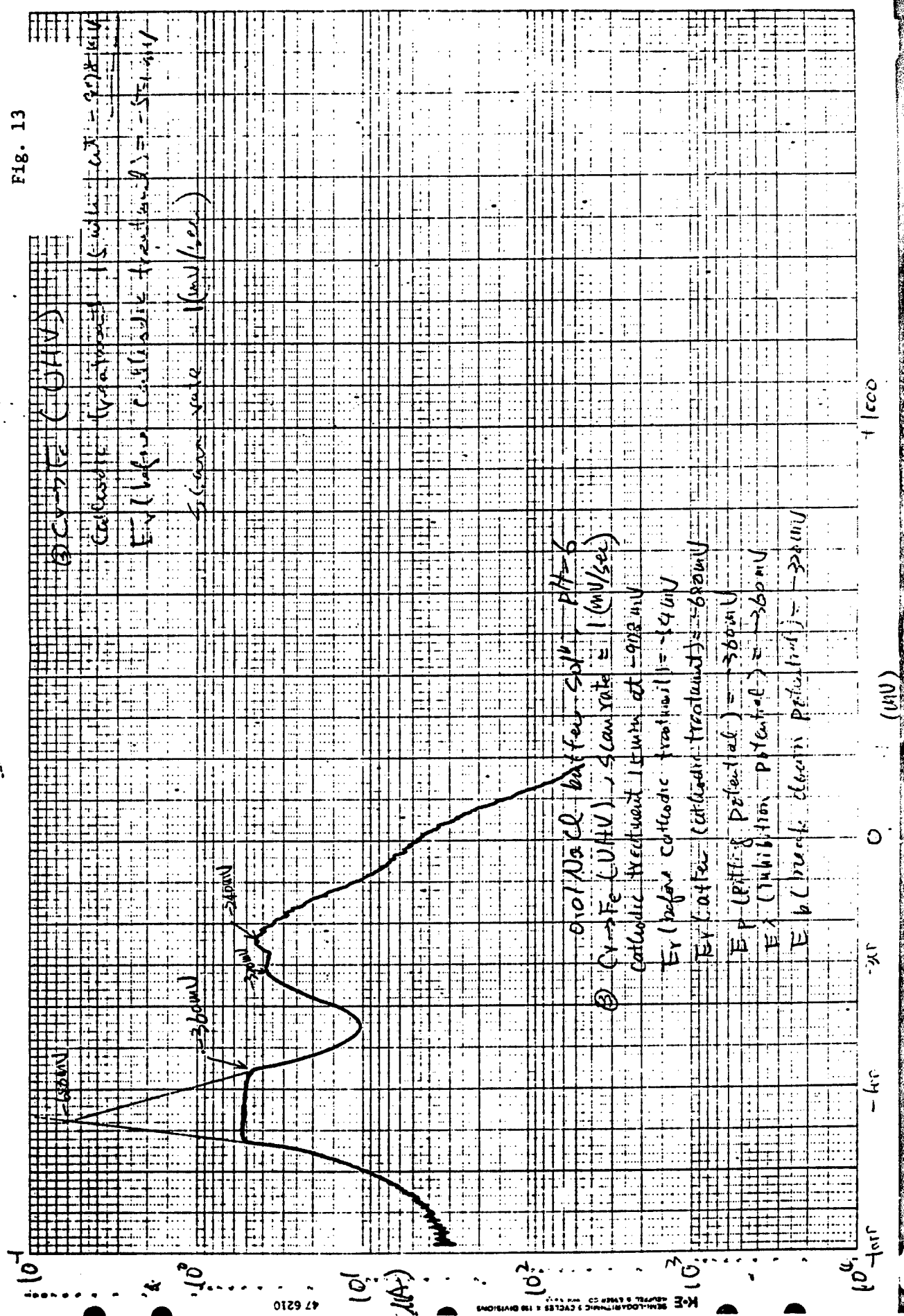


Fig. 13.

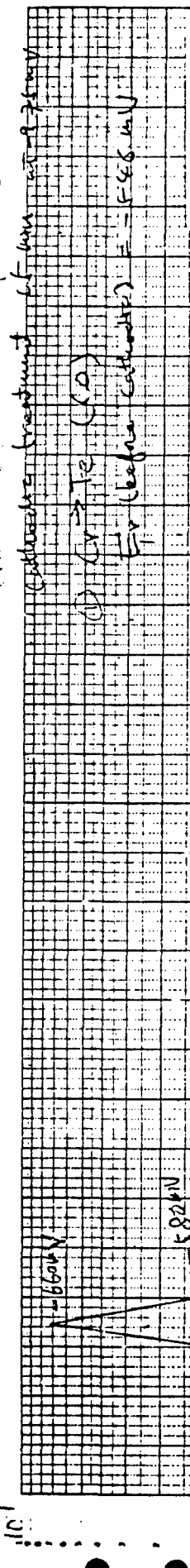


Fig. 14

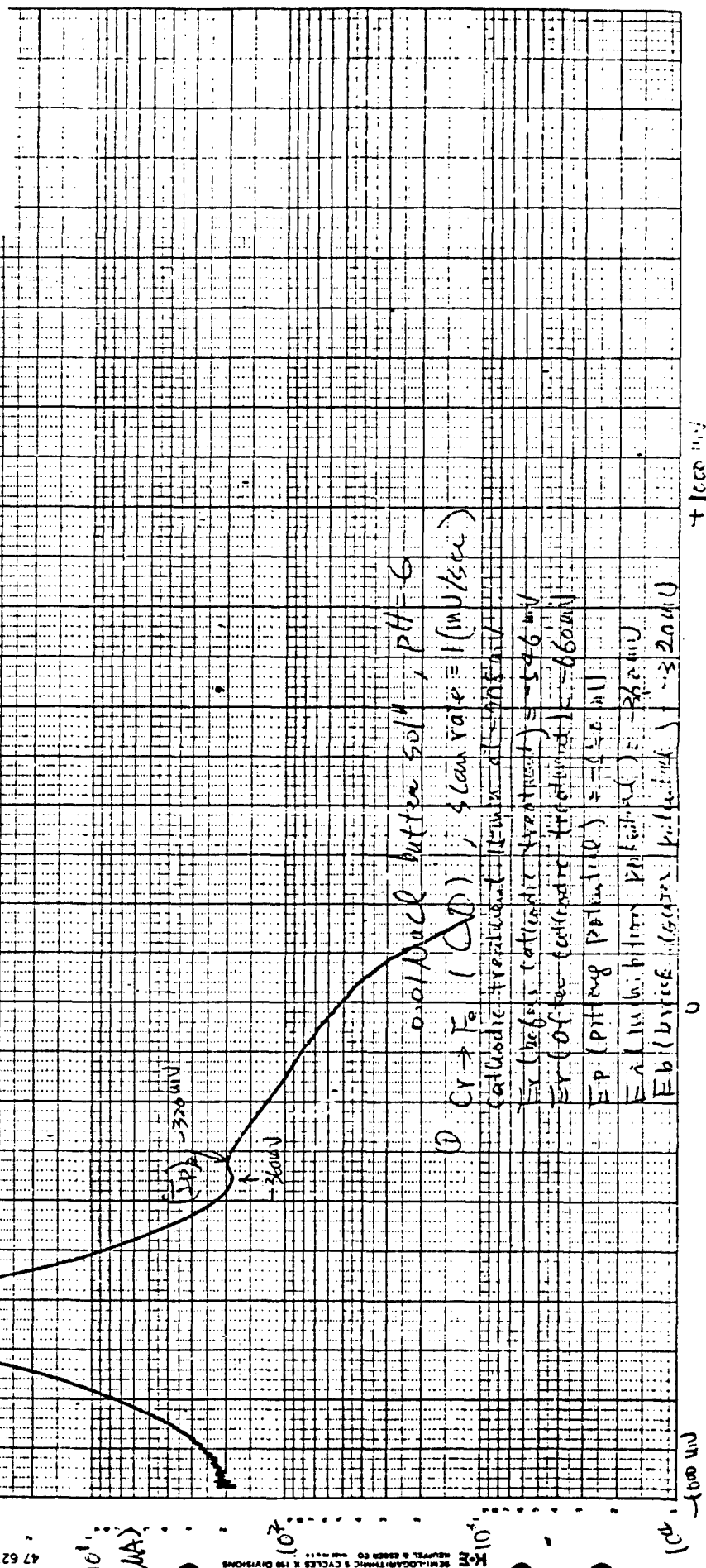


Fig. 14.

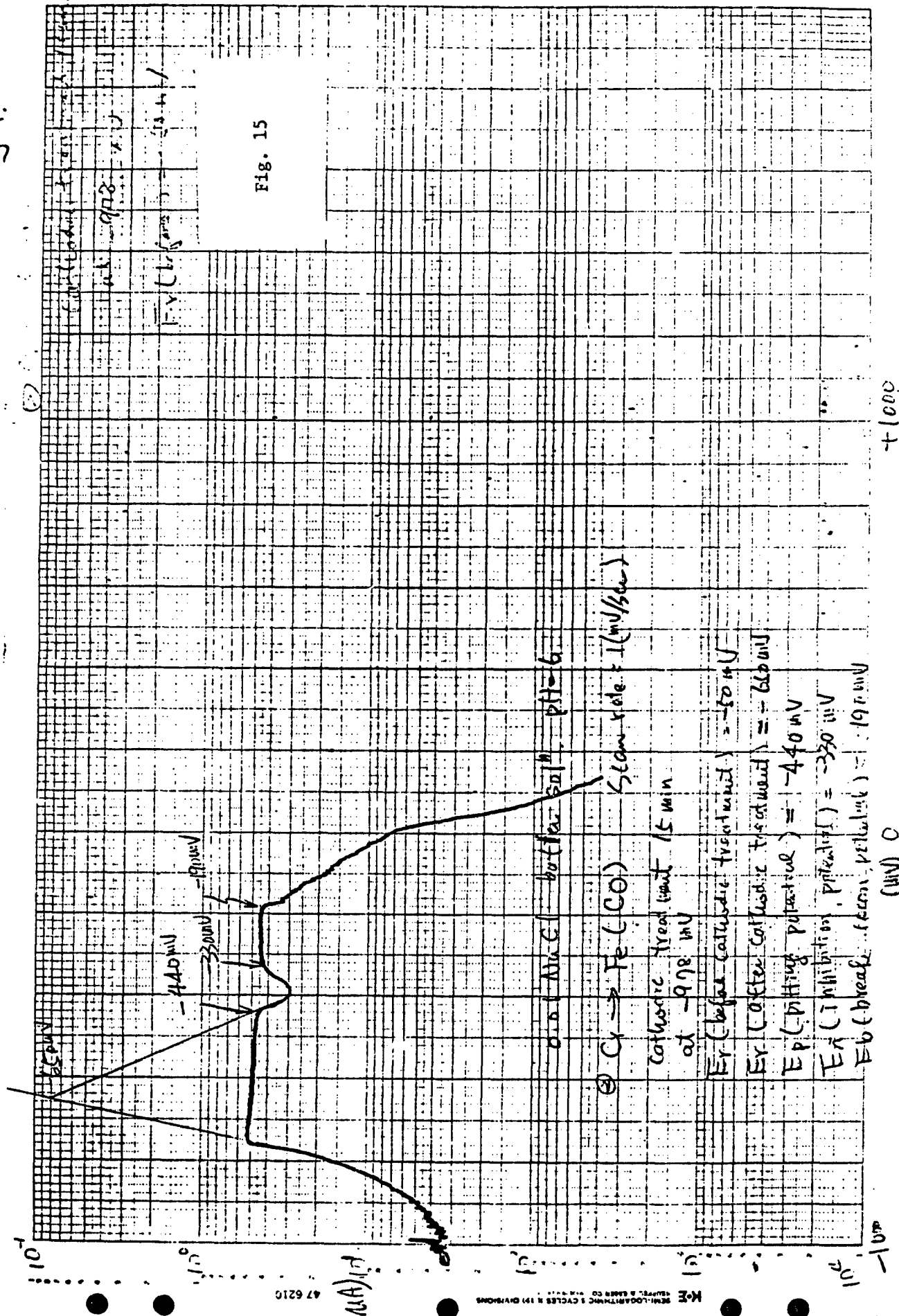


Fig. 15

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③  $\text{Cr} \rightarrow \text{Fe}(\text{CO})$  Scan rate = 1 (mV/sec)

Cathodic treatment 15 min at -98 mV

$E_r$  (before cathodic treatment) = -50 mV

$E_r$  (after cathodic treatment) = -60 mV

$E_p$  (pitting potential) = -440 mV

$E_a$  (inhibition potential) = -330 mV

$E_b$  (breakdown potential) = -190 mV

(mV) 0

+1000